Journal of Statistical Physics, Vol. 20, No. 1, 1979

The Fluctuation-Dissipation Theorem for Contracted Descriptions of Markov Processes

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Received August 24, 1978

It is shown that if the Onsager–Casimir relations and the fluctuation-dissipation theorem are valid for a stationary, Gaussian, Markov process in an N-dimensional space, then these relations are valid when the process is projected into a subspace of the original space. Both time-reversal-even and time-reversal-odd variables are allowed. Previous derivations of the fluctuation-dissipation theorem for Brownian motion from fluctuating hydrodynamics are special cases of the present result. For the Brownian motion problem, the fluctuation-dissipation theorem is proven for the case of a compressible, thermally conducting fluid with a nonlocal equation of state. Arbitrary slip boundary conditions are considered as well.

KEY WORDS: Fluctuation-dissipation theorem; Onsager–Casimir relations; contracted description; Brownian motion.

1. INTRODUCTION

In recent years a number of authors have derived a generalized Langevin equation for Brownian motion starting from linearized fluctuating hydrodynamics. In these derivations the motion of a particle immersed in a fluid is first described by linearized hydrodynamic equations for the fluid which are coupled through boundary conditions at the particle–fluid interface to Newton's equations for the particle. Random fluctuating forces are added to the hydrodynamic equations in an attempt to include a remnant of the statistical foundation of these equations. The stochastic properties of these forces are specified by means of the fluctuation-dissipation theorem (FDT), which relates these stochastic properties to the phenomenological coefficients appearing in the hydrodynamic equations.

To derive a Langevin equation for the Brownian motion of the particle, the fluid variables are eliminated from the description. In this way it is said

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0022-4715/79/0100-0057$03.00/0 © 1979 Plenum Publishing Corporation

that the description has been contracted. The elimination is accomplished by solving for the fluid variables when the particle motion is given. The resulting flow is then used to compute the forces and torques acting on the particle which are caused by the fluid motion. Having done that, it is possible to write Newton's equations for the particle without explicit reference to the fluid degrees of freedom. If there are fluctuating forces in the original equations, then modified fluctuating forces will be present in the contracted equations. In addition, solving for the fluid variables in terms of a given particle motion introduces an element of history into the description in the form of memory functions. What is discussed in this work is a proof of the contracted FDT which relates the stochastic properties of the modified fluctuating forces of the contracted description to the memory functions appearing in the contracted description. The point of this discussion is the demonstration that contracted FDT can be derived when any stationary, Gaussian, Markov process is contracted, as long as the FDT and the Onsager–Casimir relations (OCR) hold for the original description of the process. We believe that the use of the OCR in this context is new, and that the contracted FDT has not before been proven for the more general processes considered here.

Previously, the contracted FDT has been derived for a particle in a fluctuating fluid with various special boundary conditions and special constraints on the fluid. Fox and Uhlenbeck[1] proved the FDT for Brownian motion in an incompressible isothermal fluid when the motion is slow enough to allow inertial terms to be neglected; stick boundary conditions were used. Hauge and Martin-Löf[2] extended the Fox–Uhlenbeck results to include inertial effects, again with stick boundary conditions in an incompressible fluid. Bedeaux and Mazur[3] also proved the FDT in this situation, using Fourier transforms. Later Velarde and Hauge[4] proved the FDT for slip boundary conditions. Chow and Hermans[5] proved the theorem in a compressible but isothermal fluid for stick boundary conditions; and Bedeaux *et al.*[6] proved the theorem in an incompressible fluid for arbitrary slip boundary conditions.

In each of the papers cited above one of the steps used to prove the contracted FDT involves the use of Green's reciprocal theorem to establish a connection between contracted and noncontracted fluctuating forces. In each case this Green's theorem, or reciprocal theorem, is proven by appeal to the special conditions of the problem considered. It has apparently not been recognized until now that this theorem is a consequence of the OCR. That this is so is shown in Section 2, where the OCR are discussed in a more general context than fluctuating hydrodynamics. A generalized Green's theorem is established [Eq. (18)] of which the Green's theorems used in Refs. 1–6 are special cases.

Fox and Uhlenbeck pointed out that fluctuating hydrodynamics uses variables some of which are *even* under the time reversal (α-variables) and others of which are *odd* under time reversal (β-variables). For this reason Fox and Uhlenbeck derived fluctuating hydrodynamics by assuming it to be a stationary, Gaussian Markov process; they pointedly did not make use of arguments based on microscopic reversibility. Subsequent papers[2–6] also make no explicit use of microscopic reversibility and the OCR. Our general proof of the reciprocal theorem, which is used in Section 3 to prove the contracted FDT, shows that even though the matrix of phenomenological coefficients is not symmetric, it is still possible to exploit the property of microscopic reversibility as it is manifested in the OCR.

In Section 3 it will be shown that if the OCR and the FDT are valid for a set of linear fluctuating equations which describe a stationary, Gaussian Markov process, then the FDT and the OCR continue to be valid for equations which are contracted from the original equations. In addition, restrictions on the contraction process which are required for the validity of the FDT will be discussed. To a certain extent, a proof of the FDT in the generality considered here was given by Fox and Uhlenbeck. They showed that when a stationary, Gaussian Markov process is contracted according to an Enskog procedure, (1) the resulting process is also stationary and Markovian, and (2) the FDT for the contracted process holds to lowest order in the Enskog parameter. We show that in general the contracted description is non-Markovian; thus our proof of the FDT represents a generalization of the Fox–Uhlenbeck result to all orders in the Enskog parameter.

In Section 4 we consider the special case of Brownian motion in the context of the general contraction procedure described in Sections 2 and 3. The contracted FDT is proven for a particle in a compressible, thermally conducting fluid with arbitrary slip boundary conditions. To extend the validity of the FDT to a fluid near its critical point, we allow the pressure to be a nonlocal functional of density fluctuations.[7] In this way, as well as by allowing for thermal conduction, we extend the validity of the FDT beyond the cases considered in Refs. 1–6.

2. GAUSSIAN, MARKOVIAN PROCESSES AND THE ONSAGER–CASIMIR RELATIONS

In this section we review some results of nonequilibrium thermodynamics. The FDT and the OCR are derived for any Gaussian Markov process that models the approach to equilibrium of a physical system. Equation (7) gives a standard formulation of the FDT, while Eq. (16) is a concise statement of the OCR. We call Eq. (16) a *local* formulation of the OCR because it states that two matrices are equal element by element. Our goal in this section is to prove Eq. (18), which we regard as a *global* formulation of the

OCR. By a global formulation we mean one that equates integrals over all time of sums of matrix elements, rather than one that equates only individual matrix elements. The global OCR given in Eq. (18) is an abstract version of the various Green's theorems used in Refs. 1–6. In Section 4 the global OCR will be translated into the language of hydrodynamics.

Let $a(t)$ be a finite-dimensional Markov process, where $a(t)$ represents the column vector $\{a_1(t), a_2(t),\dots, a_n(t)\}$. For a continuous system, the components of $a(t)$ will refer to various cells of the system. We will assume that what we say about the finite processes can also be applied to continuous processes by way of using ever smaller cells. This procedure was followed by Fox and Uhlenbeck when they derived fluctuating hydrodynamics.

The Markov process $a(t)$ is to be designed so that it simulates the approach to equilibrium of a macroscopic system. This means that the averages $\langle a(t)\rangle$ and $\langle a(t)a(t+s)^T\rangle$ must equal the corresponding averages of these variables in thermal equilibrium as t tends to infinity. Also, the equation of motion of $\langle a(t)\rangle$ must be the phenomenological equation governing the evolution of the system to be simulated. We restrict ourselves to linear equations.

For $a(t)$ we write

$$da(t)/dt = -Ga(t) + g(t) \tag{1}$$

where G is an $N \times N$ matrix and $g(t)$ is a random N-dimensional force. We assume that $\langle g(t)\rangle = 0$, from which it follows that

$$d\langle a(t)\rangle/dt = -G\langle a(t)\rangle \tag{2}$$

Only physical systems that can be adequately described by linear phenomenological equations are to be considered. Without loss of generality we assume that $\langle a\rangle_{th} = 0$ where $\langle\cdot\rangle_{th}$ indicates the equilibrium average. The solution of Eq. (1) is given by

$$a(t) = e^{-Gt}a(0) + \int_0^t e^{-G\tau}g(t-\tau)\,d\tau \tag{3}$$

Let R and $p(s)$ be $N \times N$ matrices given by

$$R \equiv \langle aa^T\rangle_{th} \qquad \text{and} \qquad p(s) = \langle a(0)a(s)^T\rangle_{th}$$

Then asymptotic consistency requires

$$\lim_{t\to\infty} \langle a(t)\rangle_g = \langle a\rangle_{th} = 0 \tag{4a}$$

$$\lim_{t\to\infty} \langle a(t)a(t)^T\rangle_g = R \tag{4b}$$

$$\lim_{t\to\infty} \langle a(t)a(t+s)^T\rangle_g = p(s) \tag{4c}$$

Condition (4a) implies that the eigenvalues of G have positive real parts, since this condition is to hold for arbitrary initial conditions. The notation $\langle\cdot\rangle_g$ indicates an average over all random forces $g(t)$.

Because $a(t)$ is to be a stationary, Gaussian Markov process, g is delta-correlated, i.e., $\langle g(t)g(s)^T\rangle$ is given by

$$\langle g(t)g(s)^T\rangle = 2A\,\delta(t-s) \tag{5}$$

where A is another $N \times N$ matrix. Thus, condition (4b) and the solution, which is Eq. (3), imply

$$R = \int_0^\infty e^{-Gt}2Ae^{-G^Tt}\,dt \tag{6}$$

The FDT now follows by integrating Eq. (6) by parts. In this way, Eq. (6) implies

$$2A = GR + RG^T \tag{7}$$

In a similar fashion, condition (4c) implies the relation

$$Re^{G^Ts} = p(s) \tag{8}$$

Equation (8) is the Onsager regression hypothesis: the correlation function $p(s)$ decays according to the macroscopic law $\exp(-G^Ts)$.

Now consider the consequences of microscopic reversibility. We assume that the components of the vector $a(t)$ are either α-variables or β-variables. That is, they are either time-reversal-even or time-reversal-odd. Let $\alpha_j(t)$ denote even components of $a(t)$ and $\beta_i(t)$ denote odd components. Then microscopic reversibility implies the following relations[8]:

$$\langle\alpha_i(0)\beta_j(s)\rangle_{th} = -\langle\alpha_i(s)\beta_j(0)\rangle_{th} \tag{9a}$$

$$\langle\alpha_i(0)\alpha_j(s)\rangle_{th} = \langle\alpha_i(s)\alpha_j(0)\rangle_{th} \tag{9b}$$

$$\langle\beta_i(0)\beta_j(s)\rangle_{th} = \langle\beta_i(s)\beta_j(0)\rangle_{th} \tag{9c}$$

Let P_α be a projection operator onto the space spanned by the α-variables and P_β be a projection operator onto the space spanned by β-variables so that

$$P_\alpha + P_\beta = 1 \tag{10}$$

It is convenient to write $p(s) = p_{\alpha\alpha}(s) + p_{\beta\beta}(s) + p_{\alpha\beta}(s) + p_{\beta\alpha}(s)$, where

$$\begin{aligned} p_{\alpha\alpha}(s) &= P_\alpha p(s)P_\alpha; \qquad & p_{\beta\beta}(s) &= P_\beta p(s)P_\beta \\ p_{\alpha\beta}(s) &= P_\alpha p(s)P_\beta; \qquad & p_{\beta\alpha}(s) &= P_\beta p(s)P_\alpha \end{aligned} \tag{11}$$

Then the symmetry relations expressed by Eq. (9) imply the relations

$$p(s)_{\alpha\alpha} = p(s)^T_{\alpha\alpha}, \qquad p(s)_{\alpha\beta} = -p(s)^T_{\alpha\beta}, \qquad p(s)_{\beta\beta} = p(s)^T_{\beta\beta} \tag{12}$$

Note that the p matrices are $N \times N$ matrices. We emphasize that Eqs. (12) are consequences of microscopic reversibility and of the fact that the components of $a(t)$ are either α-variables or β-variables.

Because of the asymptotic consistency requirement expressed by Eq. (8), the following relations for G and R are implied by Eqs. (12):

$$(RG^T)_{\alpha\alpha} = (GR)_{\alpha\alpha} \tag{13a}$$

$$(RG^T)_{\alpha\beta} = -(GR)_{\alpha\beta} \tag{13b}$$

$$(RG^T)_{\beta\alpha} = -(GR)_{\beta\alpha} \tag{13c}$$

$$(RG^T)_{\beta\beta} = (GR)_{\beta\beta} \tag{13d}$$

The α, β subscripts are used here in the same way as they were used in Eq. (11): i.e., if M is a matrix, $M_{\alpha\beta}$ is given by $M_{\alpha\beta} = P_\alpha M P_\beta$, etc.

In the absence of a magnetic field the correlation between α and β variables vanishes; i.e., $\langle\alpha(0)\beta(0)\rangle = 0$.[8] This means that

$$R_{\alpha\beta} = R_{\beta\alpha} = 0 \tag{14}$$

In other words, the matrix R, which gives the variance of equilibrium fluctuations, does not connect α and β variables. Henceforth we denote $R_{\alpha\alpha}$ and $R_{\beta\beta}$ by R_α and R_β, respectively. Then we have

$$R = R_\alpha + R_\beta \qquad \text{and} \qquad R^{-1} = R_\alpha^{-1} + R_\beta^{-1}$$

assuming the inverses indicated exist.

In this notation Eq. (13b) becomes

$$R_\alpha G_{\alpha\beta}^T = G_{\alpha\beta} R_\beta \tag{15}$$

If we multiply Eq. (15) from the left and right by R_α^{-1} and R_β^{-1}, respectively, we have

$$G_{\alpha\beta}^T R_\beta^{-1} = R_\alpha^{-1} G_{\alpha\beta}$$

Similar steps with the other relations (13) give

$$G^T S^{-1} = S^{-1} G \tag{16a}$$

where the matrix S^{-1} is given by

$$S^{-1} = R_\alpha^{-1} - R_\beta^{-1} \tag{16b}$$

Thus Eqs. (16) represent a reformulation of the OCR in a more concise form than heretofore found in the literature. We now use these equations to prove the global OCR referred to at the beginning of this section.

The correlation between the random forces $g(t)$ is actually a generalized function—a delta function. Its properties are determined by its effects on a certain class of test functions. Our strategy for proving the contracted FDT will be to examine the action of the correlation function of the contracted fluctuating forces on a second class of test functions. These functions are chosen to be solutions of deterministic equations of motion, which are obtained by replacing the random force by a "sure" but arbitrary force. In this way information about the phenomenology is explicitly incorporated into the test functions.

Following this strategy we formulate the global form of the OCR by determining the action of S^{-1} in certain integrals. These integrals involve solutions to equations of motion derived from the fluctuating equation [Eq. (1)] by replacing the fluctuating force $g(t)$ by the "sure" but arbitrary forces $F^{(i)}(t)$.

Let $a^{(i)}(t)$, for $i = 1, 2$, be solutions of the now deterministic equation

$$da^{(i)}/dt = -Ga^{(i)}(t) + F^{(i)}(t), \qquad i = 1, 2 \tag{17}$$

where the $F^{(i)}(t)$ are nonfluctuating external forces arbitrary except for the restriction $F^{(i)}(t) = 0$ for $|t| > T_c$, where T_c is an arbitrary cutoff time and the $a^{(i)}(t)$ are assumed to vanish for $t < -T_c$.

With these conditions, the global OCR to be proven is the equality

$$\int dt\, F^{(1)}(t)^T S^{-1} a^{(2)}(T - t) = \int dt\, a^{(1)}(t)^T S^{-1} F^{(2)}(T - t) \tag{18}$$

which relates the distinct solutions of the two equations given as Eq. (17). Equation (18) is valid for all times T. (Every integration over time t in this paper extends over all time.)

The primary ingredient in the proof of Eq. (18) is the local OCR given by Eqs. (16). The Green's theorems used by the various authors mentioned in the introduction are special cases of Eq. (18).

We end this section by proving the central result: Eq. (18). Observe that because $a^{(1)}(t) = 0$ for $t < -T_c$, and because $a^{(1)}(t)$ vanishes as t approaches infinity, we have

$$0 = \int dt\, (d/dt)[a^{(1)}(t)^T S^{-1} a^{(2)}(T - t)] \tag{19}$$

To evaluate the integrand of Eq. (18), use the equation of motion given in Eq. (17):

$$\begin{aligned} 0 = &\int dt\, \{-a^{(1)}(t)^T [G^T S^{-1} - S^{-1} G] a^{(2)}(T - t)\} \\ &+ \int dt\, [F^{(1)}(t)^T S^{-1} a^{(2)}(T - t) - a^{(1)}(t)^T S^{-1} F^{(2)}(T - t)] \end{aligned} \tag{20}$$

The global OCR [Eq. (18)] follows immediately from Eqs. (20) and (16a) (the local form of the OCR).

Note that no restrictions were required on the force $F^{(2)}(t)$. In particular, $F^{(2)}(t)$ could be replaced by the fluctuating force $g(t)$ of Eq. (1). Also note that Eq. (18) is an equality between two convolutions and is easily expressed in terms of Fourier transforms. It is used in this way by Bedeaux and Mazur[3] and Chow and Hermans.[5] In our statement of the FDT we will not need to worry about the propriety of Fourier-transforming a fluctuating force.

3. CONTRACTION AND THE FLUCTUATION-DISSIPATION THEOREM

In this section it is shown that if the global OCR [Eq. (18)] and the FDT [Eq. (7)] are true for the process described by Eq. (1), then modified versions of these theorems hold in a contracted description of the process. The demonstration of this fact is possible because the formal statement of the global OCR allows the methods of Hauge and Martin-Löf[2] to be generalized.

First the FDT for the noncontracted description is written in a global form. Then the contraction is introduced and suitably restricted. Finally, the global OCR and the FDT in the original description are shown to yield the FDT for the contracted description. The contracted process is non-Markovian, or at least nonstationary.[2] We believe that the restrictions on the contraction which are sufficient to prove the contracted FDT are stated here for the first time.

By contracting we mean considering only a subspace of the N-dimensional space of which $a(t)$ is an element. That is, we restrict our attention to $n < N$ components of $a(t)$. Since the time evolution of $a(t)$ is governed by a linear equation, it is possible to solve for those components that we do not want to retain in the description in terms of the remaining components of $a(t)$. The result is used to write a linear equation for the n components of $a(t)$ that are retained in terms of these components alone. Because $a(t)$ is determined by a differential equation, the resulting equation will exhibit memory effects. The contraction procedure is best described using projection operators.

Let P be a time-independent projection operator and let Q be its complement. The projection P defines the n components of $a(t)$ that are to be retained, the so-called relevant components. The null space of P is the space spanned by the so-called irrelevant variables. Let $b^{(i)}(t)$ and $b(t)$ be given by

$$b^{(i)}(t) = Pa^{(i)}(t); \qquad b(t) = Pa(t) \tag{21}$$

where i is either 1 or 2.

[2] See Fox[9] for a discussion of the nonstationary aspect of the contracted description.

The procedure described above yields equations of the following form for $b^{(i)}(t)$ and $b(t)$:

$$db^{(i)}(t)/dt = -\Omega b^{(i)}(t) - \int \Gamma(t - s)b^{(i)}(s)\, ds + f^{(i)}(t) \tag{22a}$$

$$db(t)/dt = -\Omega b(t) - \int \Gamma(t - s)b(s)\, ds + h(t) \tag{22b}$$

The quantities Ω and $\Gamma(t)$ are $N \times N$ matrices such that

$$P\Omega P = \Omega \qquad \text{and} \qquad P\Gamma(t)P = \Gamma(t) \tag{23}$$

If the force F has no components in the irrelevant subspace, i.e., if $QF^{(i)} = 0$, then $f^{(i)}$ is given by

$$f^{(i)} = PF^{(i)}$$

However, since $g(t)$ is a random force, it cannot be assumed that Qg vanishes or that $h(t)$ is simply the P projection of $g(t)$. We require that $\Gamma(t)$ vanish for t less than zero.

We will prove the FDT for the contracted process in the following local form:

$$\begin{aligned}\langle h(0)h(t - s)^T\rangle &= \langle h(s - t)h(0)^T\rangle = \langle h(s)h(t)^T\rangle \\ &= \delta(t - s)[S_p\Omega^T R_p^{-1}S_p + S_pR_p^{-1}\Omega S_p] \\ &\quad + S_p[\Gamma^T(s - t)R_p^{-1} + R_p^{-1}\Gamma(t - s)]S_p\end{aligned} \tag{24}$$

where $R_p^{-1} = PR^{-1}P$ and $S_p = PSP$. To prove this equation it is sufficient to require that (a) the projection P commute with the projections P_α and P_β, and (b) P commute with R. Condition (a) means that the projected variables, i.e., the relevant variables, must have a definite symmetry with respect to time reversal. Condition (a) would be violated, for example, if we chose a relevant variable to be a sum of an α-variable and a β-variable. Since the components of $a(t)$ were required to have a definite time-reversal symmetry, it is only natural to require that the projected variables also have this property.

Condition (b) means that if two variables are correlated in thermal equilibrium, it is not allowed to designate only one of them as a relevant variable. Condition (b) also means that a relevant variable cannot be a linear combination of variables that are uncorrelated in thermal equilibrium. If either condition (a) or (b) is violated, it is still possible to derive the contracted equations of motion, but there will be no guarantee that the contracted FDT is valid. We believe that conditions (a) and (b) for the validity of the contracted FDT have not been described before. Of course, these conditions are fulfilled in the Brownian motion problems considered in Refs. 1–6. However, none of these articles treated the problem of contracting linear fluctuating equations and the requirements for preserving the FDT in the generality we treat the problem here. As mentioned in the introduction, Fox and Uhlenbeck[1] did show that when Eq. (1) is contracted according to a Chapman–Enskog-like procedure, the contracted equation is Markovian to lowest order and that the FDT holds to lowest order in the expansion parameter. Our result generalizes that result to all orders in the Chapman–Enskog parameter and elucidates the role of time-reversal symmetry in deriving the complete contracted FDT.

We know of two ways to prove the contracted FDT given conditions (a) and (b). The first is to find explicit expressions for Ω, $\Gamma(t)$, and $h(t)$ in terms of Q, P, G, and $g(t)$. This procedure is essentially that used in proofs of the FDT which follow Zwanzig–Mori projection operator methods.[10] However, we are interested here only in the FDT and its relation to the OCR. In addition, our aim is to present a proof which can be directly translated into the language of specific problems. Since explicit construction of $\Gamma(t)$ is usually quite difficult, this method is hard to use in most problems. (For the Brownian motion, Bedeaux and Mazur[3] give a proof of the FDT along these lines, but that proof is restricted to spherical particles in an incompressible fluid.) By following the method described below we generalize the methods used in Refs. 1–6 in a way which is easy to mimic in specific instances.

To prove the contracted FDT we first note that the original FDT, Eq. (7), implies the following equalities:

$$R^{-1}2AR^{-1} = R^{-1}G + G^TR^{-1} = S^{-1}2AS^{-1} \tag{25}$$

The first equality follows from Eq. (7) by multiplying by R^{-1} from the left and from the right. The second equality follows from

$$S^{-1}R = P_\alpha - P_\beta \tag{26}$$

and the local OCR, $G^TS^{-1} = S^{-1}G$, because we have

$$\begin{aligned} S^{-1}2AS^{-1} &= S^{-1}GRS^{-1} + S^{-1}RG^TS^{-1} \\ &= S^{-1}G(P_\alpha - P_\beta) + (P_\alpha - P_\beta)G^TS^{-1} \\ &= G^TS^{-1}(P_\alpha - P_\beta) + (P_\alpha - P_\beta)S^{-1}G \end{aligned} \tag{27}$$

and

$$(P_\alpha - P_\beta)S^{-1} = R^{-1} = (P_\alpha - P_\beta)^2R^{-1}$$

The local form of the FDT given in Eq. (25) implies the following global statement of the FDT:

$$\begin{aligned} &\int dt\, a^{(1)}(t)^TS^{-1}2AS^{-1}a^{(1)}(t) \\ &\quad = \int dt \int dt'\, a^{(1)}(t)^TS^{-1}\langle g(t)g(t')^T\rangle S^{-1}a^{(1)}(t') \\ &\quad = \int dt\, 2a^{(1)}(t)^TR^{-1}F^{(1)}(t) \end{aligned} \tag{28}$$

Equation (28) expresses the properties of the correlation matrix $\langle g(t)g(t')^T\rangle$ by its action in integrals against the class of test functions $a^{(i)}(t)$ which are solutions of the arbitrary but "sure" equations of motion given in Eq. (17). Equation (24) will be proven by determining the action of $\langle h(t)h(t')^T\rangle$ in integrals against the text functions $b^{(i)}(t)$ which are solutions of the "sure" equations given in Eq. (22a).

To prove Eq. (28) note that because $a^{(1)}(t)$ vanishes for t less than $-T_c$ and because $a^{(1)}(t)$ vanishes as t tends to infinity, the integral below vanishes, i.e.,

$$\int dt\,(d/dt)[a^{(1)}(t)^T R^{-1} a^{(1)}(t)] = 0 \tag{29}$$

The equality of the first and last integrals in Eq. (28) follows from Eq. (29) by using the equations of motion to carry out the differentiation indicated and then applying the local form of the FDT. The second integral is equal to the first because of Eq. (5).

In Appendix A it is shown that if conditions (a) and (b) are satisfied in the form

$$[P, P_\alpha] = [P, P_\beta] = [P, R^{-1}] = 0 \tag{30}$$

then the OCR for the contracted description hold in the form

$$\Omega^T S_p^{-1} = S_p^{-1}\Omega \tag{31a}$$

$$\Gamma^T(t) S_p^{-1} = S_p^{-1}\Gamma(t) \tag{31b}$$

If $P = 1$, then $\Gamma(t)$ vanishes and Ω is just G. In this way the original local OCR are contained in the contracted local OCR. Hauge and Martin-Löf proved the contracted local OCR for the special case of Brownian motion in an isothermal, incompressible fluid. In that case all the variables are β-variables since the temperature and pressure are fixed. Here both α and β variables are allowed.

With the contracted form of the local OCR, Eq. (31), it is possible to relate the contracted fluctuating force $h(t)$ to the original fluctuating force $g(t)$. This relationship and the global FDT given in Eq. (28) yield a proof of the contracted FDT. In Appendix B the following reciprocal theorem is proven:

$$\int dt\, h(t)^T S_p^{-1} b^{(2)}(T-t) = \int dt\, g(t)^T S_p^{-1} a^{(2)}(T-t) \tag{32}$$

provided $PF^{(2)} = f^{(2)} = F^{(2)}$. Both $a^{(2)}(t)$ and $b^{(2)}(t)$ are nonfluctuating quantities.

To derive the contracted global FDT from this last equation, form the double integral

$$I = \int dt \int dt\, b^{(2)}(T-t)^T S_p^{-1}\langle h(t)h(s)^T\rangle S_p^{-1} b^{(2)}(T-t) \tag{33}$$

The reciprocal theorem, Eq. (32), the relation between A and the stochastic properties of $g(t)$ given in Eq. (5), and the global FDT given in Eq. (28) imply that I is also given by

$$I = 2 \int dt\, a^{(2)} R^{-1} F^{(2)}(t) \tag{34}$$

Since we have $F^{(2)} = PF^{(2)} = f^{(2)}$ by assumption, and since $[P, R^{-1}] = 0$, it follows that

$$\begin{aligned} I &= 2 \int dt\, b^{(2)}(t)^T R_p^{-1} f^{(2)}(t) \\ &= \int ds \int dt\, b^{(2)}(T - t)^T S_p^{-1} \langle h(t) h(s)^T \rangle S_p^{-1} b^{(2)}(T - t) \end{aligned} \tag{35}$$

Equation (35) is the global form of the contracted FDT. It is the contracted analog of Eq. (28). The local form of the contracted FDT, Eq. (24), can be derived from the global form by using the equation of motion for $b^{(2)}(t)$ to express $f^{(2)}(t)$ in terms of Ω, $\Gamma(t)$, and $b^{(2)}(t)$. The equation of motion gives for the "sure" force $f^{(2)}(t)$

$$f^{(2)}(t) = db^{(2)}(t)/dt + \Omega b^{(2)}(t) + \int ds\, \Gamma(t - s) b^{(2)}(s) \tag{36}$$

Substituting for $f^{(2)}(t)$ in Eq. (35) gives

$$\begin{aligned} I = 2 \int dt\, &[b^{(2)}(t) R_p^{-1}\, db^{(2)}(t)/dt] \\ &+ \int dt \int ds \{\delta(t - s) b^{(2)}(t) [\Omega^T R_p^{-1} + R_p^{-1} \Omega] b^{(2)}(s) \\ &+ b^{(2)}(t) [\Gamma^T(s - t) R_p^{-1} + R_p^{-1} \Gamma(t - s)] b^{(2)}(s)\} \end{aligned} \tag{37}$$

The first line of this equation vanishes because $b^{(2)}(t)$ vanishes at $t = \infty$. Observe that $b^{(2)}(t)$ is arbitrary since it is driven by the arbitrary force $PF^{(2)}$. Because $b^{(2)}(t)$ is arbitrary, Eqs. (35) and (37) imply

$$\begin{aligned} S_p^{-1} \langle h(T - t) h(T - s)^T \rangle S_p^{-1} &= \delta(t - s)(\Omega^T R_p^{-1} + R_p^{-1} \Omega) \\ &\quad + \Gamma^T(s - t) R_p^{-1} + R_p^{-1} \Gamma(t - s) \end{aligned} \tag{38}$$

Multiplying both sides of this equation by S_p gives the local form of the contracted FDT, Eq. (24). The time T is also arbitrary and can be chosen to be t, s, or $t + s$. When P is the identity, $\Gamma(t)$ vanishes and the contracted FDT becomes identical with the noncontracted FDT. This completes the derivation of the contracted FDT, Eq. (24).

The noncontracted FDT, Eq. (25), implies that

$$2A = SR^{-1}2AR^{-1}S = (P_\alpha - P_\beta)2A(P_\alpha - P_\beta) \qquad \text{and} \qquad 2A_{\alpha\beta} = -2A_{\alpha\beta} \tag{39}$$

This means that $A_{\alpha\beta}$ vanishes and that there is no correlation between random forces associated with variables of different time-reversal symmetry. This is no longer the case in the contracted description. Using the relation $R_p^{-1}S_p = P(P_\alpha - P_\beta)P$ and the local OCR for Ω we can multiply the contracted FDT from the left by P_α and from the right by P_β to find

$$P_\alpha\langle h(0)h(t-s)^T\rangle P_\beta = -R_\alpha\Gamma^T_{\alpha\beta}(s-t) - \Gamma_{\alpha\beta}(t-s)R_\beta \tag{40}$$

The local OCR for $\Gamma(t)$ relates $\Gamma(t-s)$ to $\Gamma^T(s-t)$, not to $\Gamma^T(t-s)$. Hence we have

$$P_\alpha\langle h(0)h(t-s)^T\rangle P_\beta = [\Gamma_{\alpha\beta}(s-t) - \Gamma_{\alpha\beta}(t-s)]R_\beta \tag{41}$$

Recalling that $\Gamma(t)$ vanishes for negative times, we see that the force correlation function depends on the sign of $t - s$ as well as its magnitude and that there is correlation between forces associated with different time-reversal symmetry in the contracted description.

4. FLUCTUATING HYDRODYNAMICS AND BROWNIAN MOTION

In this section we apply the considerations of the last two sections to the proof of the FDT for a particle submerged in a fluctuating, compressible, and thermally conducting fluid. Our method of proof allows for correlated density fluctuations at distinct points in the fluid as is required for the description of a fluid near its critical point. We do not allow for singular mass or entropy density at the particle–fluid interface, but we do allow a singular energy density there. The resulting surface effects do not affect the particle motion in the absence of interfacial mass density.

This work differs from the work of Bedeaux *et al.*[6] in that the contracted FDT is proven without explicit construction of fluctuating forces which satisfy the noncontracted FDT. We do not introduce fluctuating surface forces as do Bedeaux *et al.* because our aim is to show only that *if* fluctuating forces can be found which satisfy the noncontracted FDT, and *if* boundary conditions are consistent with microscopic reversibility, then the contracted FDT follows. By proving the contracted FDT without explicitly constructing fluctuating forces it is hoped that the role of microscopic reversibility will be exhibited more plainly. Microscopic reversibility as expressed by the global OCR, Eq. (18), is here regarded as a constraint on boundary conditions and constitutive relations sufficient to guarantee the validity of the contracted FDT. This work also differs from earlier work in that we determine the matrix of correlations from fluctuations of the entropy itself rather than from the rate of entropy production. For the sake of completeness we do finally present fluctuating forces which ensure the validity of the noncontracted FDT.

We will show in this section how the general formulation of the last two sections can be expressed in terms of the specific language of linearized hydrodynamics. In this way it is shown how the proofs of the FDT given in Refs. 1–6 are special cases of the proof given in Section 3.

The linearized hydrodynamic equations for a fluid-plus-particle system are

$$\partial\delta\rho/\partial t = \rho_0 \nabla\cdot\mathbf{u} \tag{42a}$$

$$\rho c_v \, \partial\delta T/\partial t = (\alpha T_0/\chi_T) \nabla\cdot\mathbf{u} - \nabla\cdot\mathbf{q} - \nabla\cdot\mathbf{g} \tag{42b}$$

$$\rho_0 \, \partial\mathbf{u}/\partial t = \nabla\cdot\mathsf{P} + \nabla\cdot\mathsf{s} \tag{42c}$$

$$m \, d\mathbf{U}/dt = -\int dS \, [\hat{\mathbf{n}}\cdot\mathsf{P} + \hat{\mathbf{n}}\cdot\mathsf{s}] + \mathbf{F}(t) \tag{42d}$$

$$\mathsf{J}\cdot d\boldsymbol{\Omega}/dt = -\int dS \, [\mathbf{r} \times (\mathsf{P} + \mathsf{s})\cdot\hat{\mathbf{n}}] + \mathbf{M}(t) \tag{42e}$$

In these equations ρ_0 and T_0 are equilibrium values of the density and temperature of the fluid: $\delta\rho$ and δT are small deviations of the density and temperature from ρ_0 and T_0, respectively. The stress tensor is denoted by P. It can be written as

$$P_{ij} = -(p_0 + \delta p)\delta_{ij} + \sigma_{ij} \tag{43}$$

where p_0 is the equilibrium pressure and δp denotes deviations from p_0. Since the constant pressure p_0 does not contribute to the equations of motion, we will henceforth use ρ, T, and p for $\delta\rho$, δT, and δp. The pressure p is to be determined from the equation of state of the fluid in terms of ρ and T. Normally p is given by a local equation

$$p(\mathbf{r}, t) = \alpha T(\mathbf{r}, t)/\chi_T + \rho(\mathbf{r}, t)/(\rho_0\chi_T) \tag{44}$$

where χ_T is the isothermal compressibility and α is the coefficient of thermal expansion in the fluid. However, in a fluid near its critical point, the equation of state may be nonlocal. Then p will be given by an equation of the form

$$p(\mathbf{r}, t) = (\alpha/\chi_T)T(\mathbf{r}, t) + \rho_0 \int Q(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}'t) \, d^3r \tag{45}$$

where $Q(r, r')$ describes the correlation of density fluctuations.[11] In this section, volume integrals will be understood to be over the volume of the fluid outside the particle, and surface integrals will be understood as ranging over the particle surface. It is consistent with the linearization to neglect the motion of the particle in the surface and volume integration limits.[2] The vector $\hat{\mathbf{n}}$ points normal from the fluid into the particle. We assume the fluid to be only bounded by the particle surface. Integrands will all be assumed to vanish at infinity.

The stress tensor σ and the heat flux vector $\mathbf{q}$ must be determined by phenomenological constitutive relations. These will be specified later. The quantities s_{ij} and g_i are random stresses and heat fluxes. The divergences of these quantities play the role of the random forces $g(t)$ in Sections 2 and 3. The heat capacity per unit mass at constant volume is denoted by c_v; $\mathbf{U}$ is the velocity of the Brownian particle and $\mathbf{\Omega}$ is its angular velocity. The mass of the particle is m and J is its inertia tensor. External forces and torques are denoted by $\mathbf{F}$ and $\mathbf{M}$. In writing Eq. (42) we implicitly assume that there is no surface momentum, mass, or entropy density. On the other hand, depending on the boundary conditions, there may be surface entropy production.

The hydrodynamic equations involve linear differential operators, whereas the equations of motion in Sections 2 and 3 involve only finite-dimensional matrix operators. By imagining the fluid to be divided into many small cells and replacing derivatives by finite differences, the proof of the FDT given above can be applied to the present case. The position variable $\mathbf{r}$ acts here as another label for the components of the vector $a(t)$.

The equations of motion must be completed by specifying boundary conditions. These will be given below along with the constitutive relations. The deterministic equations analogous to Eq. (42) which yield solutions appropriate for use in the global OCR and FDT are found simply by setting s and $\mathbf{g}$ equal to specified functions $\mathsf{s}^{(i)}$ and $g^{(i)}$. We will assume $\mathsf{s}^{(i)}$ and $g^{(i)}$ vanish at the particle surface. In the deterministic case, $\mathbf{F} = \mathbf{F}^{(i)}$, $\mathbf{M} = \mathbf{M}^{(i)}$.

The first task in applying the scheme described in Sections 2 and 3 is to determine the matrix of equilibrium correlations R. In previous work on this subject the matrix R has been determined from the rate of entropy production, which in turn is found from the rate of energy dissipation.[1–6] In general, there will be entropy production at the fluid–particle interface which depends on the precise nature of the boundary conditions. Velarde and Hauge[4] were able to extend the results of Hauge and Martin-Löf[2] to the case of slip boundary conditions precisely because in both the stick and slip cases there is no surface entropy production. This is the unrecognized accidental feature of these cases referred to by Velarde and Hauge.[4] Bedeaux *et al.*[6] were able to treat the arbitrary slip case because they recognized that in that case there is a singular entropy production density at the surface.

Here we determine R directly from the entropy associated with fluctuations from equilibrium. The reason for proceeding in this way is that to prove the contracted FDT we need only show that the boundary conditions are consistent with microscopic reversibility. It is not really necessary to know *how much* entropy is produced by the fluid sliding over the particle surface, if the noncontracted FDT is assumed.

Small fluctuations of the vector $a(t)$ from equilibrium are assumed to be described by a Gaussian distribution; consistency requires that the distribution be given by

$$P(a) = C \exp[-a^T R^{-1} a/2] \tag{46}$$

This choice assures us that equilibrium correlations are given by R. On the other hand, we assume that the fluid-plus-particle system is maintained in thermal equilibrium by a heat reservoir at temperature T_0. The probability of a fluctuation is therefore given by

$$P(a) = C' \exp[-E(a)/(k_B T_0)] \tag{47}$$

where $E(a)$ is the nonnegative energy associated with the fluctuation a and k_B is Boltzmann's constant. At equilibrium E and a vanish. For small fluctuations, $E(a)$ can be expanded to second order in a, and R^{-1} can be determined by comparing Eqs. (46) and (47). Since E is a minimum in equilibrium, R^{-1} is found to be

$$R_{ij}^{-1} = (1/k_B T_0)\, \partial^2 E/\partial a_i\, \partial a_j \tag{48}$$

In the fluid-plus-particle system the variation of E from equilibrium at constant volume is given by

$$2E = \int d^3r\, [\delta^{(2)}(\rho e) + \rho \mathbf{u}^2] + m\mathbf{U}^2 + \mathbf{\Omega}\cdot\mathbf{J}\cdot\mathbf{\Omega} \tag{49}$$

where $\delta^{(2)}(\rho e)(r)$ is the second-order local deviation of the internal energy of the fluid from equilibrium. Near a critical point it is expected that density fluctuations will be correlated over macroscopic distances. We therefore write $\delta^{(2)}(\rho e)$ as

$$\delta^{(2)}(\rho e)(\mathbf{r}) = \frac{\rho_0 c_v}{T_0} T(\mathbf{r})^2 + \int K(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\rho(\mathbf{r}')\rho(\mathbf{r}'')\, d^3r'\, d^3r'' \tag{50}$$

That the kernel $K(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ may be nonvanishing for $r' \neq r''$ means that there is a possibility of correlated density fluctuations at distinct points. That $K(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ depends on $\mathbf{r}$ allows for the fact that a fluid containing a particle is not homogeneous. Nonlocal equations of state of this type are discussed by Gitterman and Kontorovich.[11] A kernel which gives rise to nonhomogeneous fluctuations is discussed by Lubensky and Rubin[12] in the context of mean field theory for a spin system when there is a bounding surface. Following Gitterman and Kontorovich,[11] we assume only local correlation for temperature fluctuations. The kernel K is introduced here only to show that such a generalized equation of state is easily treated in the context of our proof of the FDT.

Pressure fluctuations are related to density and temperature fluctuations by[11]

$$p(\mathbf{r}) = p_0 \frac{\delta F}{\delta \rho(\mathbf{r})} + \frac{\alpha}{\chi_T} \delta T(r) = \int Q(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')\, d^3r' + \frac{\alpha}{\chi_T} T(\mathbf{r}) \tag{51}$$

where $Q(\mathbf{r}', \mathbf{r}'')$ is given by

$$Q(\mathbf{r}', \mathbf{r}'') = \int d^3r\, K(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \tag{52}$$

If there is a singularity in the pressure at the particle surface, it cannot contribute to the particle motion because the momentum density is nonsingular.

In the case of a particle in a fluid we identify the vector of $a(t)$ of Sections 2 and 3 as

$$a(t) = \{\rho(\mathbf{r}, t), T(\mathbf{r}, t), \mathbf{u}(\mathbf{r}, t), \mathbf{U}(t), \mathbf{\Omega}(t)\} \tag{53}$$

The components of the vector $a(t)$ are thus specified by two labels: the spatial variable $\mathbf{r}$ and one of ρ, T, u_i, U_i, or Ω_i, where $i = 1, 2, 3$.

Combining Eqs. (49) and (50) and comparing Eq. (46) with Eq. (47) gives

$$k_B T R^{-1} = \begin{bmatrix} Q(\mathbf{r}, \mathbf{r}') & 0 & 0 & 0 & 0 \\ 0 & (\rho_0 c_v/T_0)\,\delta(\mathbf{r} - \mathbf{r}') & 0 & 0 & 0 \\ 0 & 0 & \rho_0 \mathsf{1}\,\delta(\mathbf{r} - \mathbf{r}') & 0 & 0 \\ 0 & 0 & 0 & M\mathsf{1} & 0 \\ 0 & 0 & 0 & 0 & \mathsf{J} \end{bmatrix} \tag{54}$$

Since the fields $\rho(\mathbf{r}, t)$ and $T(\mathbf{r}, t)$ are α-variables and $U(\mathbf{r}, t)$, $\mathbf{U}(t)$, and $\mathbf{\Omega}(t)$ are β-variables, S^{-1} is given by

$$k_B T_0 S^{-1} = k_B T_0 (R_\alpha^{-1} - R_\beta^{-1})$$

$$= \begin{bmatrix} Q(\mathbf{r}, \mathbf{r}') & 0 & 0 & 0 & 0 \\ 0 & (\rho_0 c_v/T_0)\delta(\mathbf{r} - \mathbf{r}') & 0 & 0 & 0 \\ 0 & 0 & -\rho_0 \mathsf{1}\,\delta(\mathbf{r} - \mathbf{r}') & 0 & 0 \\ 0 & 0 & 0 & -m\mathsf{1} & 0 \\ 0 & 0 & 0 & 0 & -\mathsf{J} \end{bmatrix} \tag{55}$$

This completes the specification of R^{-1} and S^{-1}.

Equations (42) can be solved when the driving forces $\nabla \cdot \mathbf{g}$, $\nabla \cdot \mathrm{s}$, $\mathbf{F}(t)$, and $\mathbf{M}(t)$ are given. As in Section 2, we consider two sets of driving forces (denoted by superscripts $i = 1, 2$) which vanish for $|t|$ greater than an arbitrary cutoff time T_c. In each case all fields are assumed to vanish for $t < -T_c$. In the language of Section 2 the deterministic driving forces are

$$\{0, \nabla\cdot\mathbf{g}^{(i)}/\rho c_v, \nabla\cdot\mathbf{s}^{(i)}/\rho_0, (1/m)\mathbf{F}^{(i)}(t), \mathrm{J}^{-1}\mathbf{M}^{(i)}(t)\} \tag{56}$$

where the $\mathrm{s}^{(i)}$ are assumed to vanish at the particle surface. The solutions of the equations of motion with these driving forces must satisfy the global OCR given by Eq. (18). Using our explicit expression for S^{-1}, given in Eq. (55), and the forces given in Eq. (56), we find for the global OCR

$$\begin{aligned}
&\int dt \int d^3r \left\{\nabla\cdot\mathbf{g}^{(1)}(\mathbf{r}, t)\frac{1}{T_0}T^{(2)}(\mathbf{r}, T-t) - \nabla\cdot\mathrm{s}^{(1)}(\mathbf{r}, t)\cdot u^{(2)}(\mathbf{r}, T-t)\right\}\\
&\qquad - \int dt\,\{\mathbf{F}^{(1)}(t)\cdot\mathbf{U}^{(2)}(T-t) + \mathbf{M}^{(1)}(t)\cdot\mathbf{\Omega}^{(2)}(T-t)\}\\
&\quad = \int dt \int d^3r \left\{T^{(1)}(\mathbf{r}, t)\frac{1}{T_0}\nabla\cdot\mathbf{g}^{(2)}(\mathbf{r}, T-t) - \mathbf{u}^{(1)}(\mathbf{r}, t)\cdot\nabla\cdot\mathrm{s}^{2}(\mathbf{r}, T-t)\right\}\\
&\qquad - \int dt\,\{\mathbf{U}^{(1)}(t)\cdot\mathbf{F}^{(2)}(T-t) + \mathbf{\Omega}^{(1)}(t)\cdot\mathbf{M}^{(2)}(T-t)\}
\end{aligned} \tag{57}$$

The kernel $Q(\mathbf{r}, \mathbf{r}')$ does not enter into Eq. (57), because there is no source term for the density in the equations of motion. Equation (57) is a consequence of microscopic reversibility. It must be valid for any proper choice of boundary conditions and constitutive relations. The appearance of the kernel Q in the equation of state means that extra boundary conditions are required to solve the equations of motion. However, we show below that the boundary condition for the density at the particle surface has no bearing on the validity of Eq. (57), whereas the boundary conditions for the temperature and the fluid velocity do influence the validity of Eq. (57). The equations of motion can be used to replace the forces appearing in the reciprocal theorem by time derivatives and flux terms. The flux terms can be integrated by parts. The time derivatives can be integrated and give vanishing results. The conclusion of these manipulations is that Eq. (57) is equivalent to the following result:

$$\begin{aligned}
&\int dt \int dS \left\{\hat{\mathbf{n}}\cdot\left[\frac{1}{T_0}\mathbf{q}^{(1)}(\mathbf{r}, t)T^{(2)}(\mathbf{r}, T-t) - T^{(1)}(\mathbf{r}, t)\frac{1}{T_0}q^{(2)}(\mathbf{r}, T-t)\right]\right.\\
&\qquad \left. + [\hat{\mathbf{n}}\cdot\mathrm{P}^{(1)}(\mathbf{r}, t)\cdot\mathbf{\Delta}^{(2)}(\mathbf{r}, T-t) - \mathbf{\Delta}^{(1)}(\mathbf{r}, t)\cdot\mathrm{P}^{(2)}(\mathbf{r}, T-t)\cdot\hat{\mathbf{n}}]\right\}\\
&\qquad + \int dt \int d^3r \left\{[\sigma_{ij}^{(1)}(\mathbf{r}, t)\,\nabla_i u_j^{(2)}(\mathbf{r}, T-t) - \nabla_i u_j^{(1)}(\mathbf{r}, t)\sigma_{ij}^{(2)}(\mathbf{r}, T-t)]\right.\\
&\qquad \left. - \frac{1}{T_0}[\mathbf{q}^{(1)}(\mathbf{r}, t)\cdot\nabla T^{(2)}(\mathbf{r}, T-t) - \nabla T^{(1)}(\mathbf{r}, t)\cdot\mathbf{q}^{(2)}(\mathbf{r}, T-t)]\right\}\\
&\quad = 0
\end{aligned} \tag{58}$$

Details are shown in Appendix C. In this equation $\mathbf{\Delta}^{(i)}(\mathbf{r}, t)$ denotes the difference between the fluid velocity and the surface velocity of the particle at the interface. It is given by

$$\mathbf{\Delta}^{(i)}(\mathbf{r}, t) = \mathbf{u}^{(i)}(\mathbf{r}, t) - \mathbf{U}^{(i)}(t) - \mathbf{\Omega}^{(i)}(t) \times \mathbf{r}, \qquad \mathbf{r} \in S, \quad i = 1, 2 \tag{59}$$

If the constitutive relations are

$$\mathbf{q}^{(i)} = -\kappa\, \nabla T^{(i)} \tag{60a}$$

$$\sigma_{ij}^{(i)} = \eta(\nabla_i u_j^{(i)} + \nabla_j u_i^{(i)} - \tfrac{2}{3}\delta_{ij}\, \nabla \cdot u^{(i)}) + \xi \delta_{ij}\, \nabla \cdot \mathbf{u}^{(i)} \tag{60b}$$

where κ is a constant thermal conductivity, η a constant shear viscosity, and ξ is a constant bulk viscosity, and if the boundary conditions are ($\mathbf{r} \in S$, $i = 1, 2$)

$$-\beta \mathbf{\Delta}^{(i)}(\mathbf{r}, t) = \hat{\mathbf{n}} \cdot \sigma^{(i)} \cdot (1 - \hat{\mathbf{n}}\hat{\mathbf{n}}) \tag{61a}$$

$$\alpha T^{(i)}(\mathbf{r}, t) = \hat{\mathbf{n}} \cdot \mathbf{q}^{(i)}(\mathbf{r}, t) \tag{61b}$$

where α and β are constants, then it is easy to see that Eq. (58), which is equivalent to the OCR, is satisfied.

The contracted FDT in this case can be proved by translating the steps leading to Eq. (24) into the present notation. Here we only note that, following Hauge and Martin-Löf, it is convenient to denote the vector

$$P \begin{bmatrix} \rho \\ T \\ \mathbf{u} \\ \mathbf{U} \\ \mathbf{\Omega} \end{bmatrix} \equiv \begin{bmatrix} 0 \\ 0 \\ 0 \\ \mathbf{U} \\ \mathbf{\Omega} \end{bmatrix} \equiv Pa(t) \tag{62}$$

by $b(t)$. This equation defines the projection P for the case of Brownian motion. The variables $\mathbf{U}$ and $\mathbf{\Omega}$ are the relevant variables. Let the operator L be $k_B T_0 R_p^{-1}$ and note that $R_p^{-1} = S_p^{-1}$. Again following Hauge and Martin-Löf,[2] we write the contracted equations of motion as

$$L\, db(t)/dt = \int \gamma(t - s) b(s)\, ds + h(t) \tag{63}$$

where $Ph(t) = h(t)$ is a fluctuating force and $P\gamma(t)P = \gamma(t)$. In the present notation the contracted FDT becomes

$$\langle h(t) h(s)^T \rangle = k_B T_0 [\gamma^T(s - t) + \gamma(t - s)] \tag{64}$$

This is formally identical to the result of Hauge and Martin-Löf,[2] but we have shown that it has wider applicability. It follows from the general considerations of Section 3 for the particular case of a compressible, thermally conducting fluid with boundary conditions consistent with microscopic reversibility.

Of course, the proof of Eq. (64) depends on the validity of the noncontracted FDT. The noncontracted FDT is established by finding fluctuating forces such that Eq. (28) is satisfied when the boundary conditions given in Eq. (61) are used. Such forces must have a singularity on the particle surface since there is dissipation there. This point is discussed by Bedeaux *et al.*[6] Suffice it to say here that we can write the fluctuating force of Eq. (28) as

$$g(t) = \left\{0, \frac{\nabla\cdot\mathbf{g}}{\rho_0 c_v}, \frac{\nabla\cdot\mathsf{s}}{\rho_0}, -\frac{1}{m}\int \mathsf{s}\cdot\hat{\mathbf{n}}\, dS, -\mathsf{J}^{-1}\int \mathbf{r}\times\mathsf{s}\cdot\hat{\mathbf{n}}\, dS\right\} \tag{65}$$

With the constitutive equations (60) and the boundary conditions (61), if $\mathbf{g}$ and s are chosen to have the following stochastic properties, then Eq. (28) will be satisfied. Write

$$\mathbf{g}(\mathbf{r}, t) = \mathbf{g}^{(1)}(\mathbf{r}, t) + \mathbf{g}^{(2)}(\mathbf{r}, t) \tag{66a}$$

where

$$\langle g^{(i)}(\mathbf{r}, t)\rangle = 0 \tag{66b}$$

$$\langle g_k^{(i)}(\mathbf{r}, t) g_l^{(j)}(\mathbf{r}', t')\rangle = \delta_{ij}\delta_{kl}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')2(k_B T_0)T_0\kappa^{(i)} \tag{66c}$$

and

$$\langle g^{(1)}(\mathbf{r}, t)\rangle = 0 \qquad \text{for } \mathbf{r}\in S \tag{66d}$$

Likewise write

$$\mathsf{s}(\mathbf{r}, t) = \mathsf{s}^{(1)}(\mathbf{r}, t) + \mathsf{s}^{(2)}(\mathbf{r}, t) \tag{67a}$$

where

$$\langle \mathsf{s}^{(i)}(\mathbf{r}, t)\rangle = 0 \tag{67b}$$

$$\begin{aligned}\langle s_{ij}^{(a)}(r, t) s_{kl}^{(b)}(r', t')\rangle &= 2k_B T_0 \delta_{ab}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')\\ &\quad\times [\eta^{(a)}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + (\xi^{(a)} - 2\eta^{(a)}/3)\delta_{ij}\delta_{kl}]\end{aligned} \tag{67c}$$

and

$$s^{(1)}(\mathbf{r}, t) = 0 \qquad \text{for } \mathbf{r}\in S \tag{67d}$$

The noncontracted FDT will be satisfied if we take

$$\begin{aligned} &\kappa^{(1)} + \kappa^{(2)} = \kappa, && \kappa^{(2)} = \alpha\\ &\eta^{(1)} + \eta^{(2)} = \eta, && \eta^{(2)} = \beta\\ &\xi^{(1)} + \xi^{(2)} = \xi \end{aligned}$$

The bulk viscosity $\xi^{(2)}$ is arbitrary.

This construction does not depend on the density boundary conditions. The arbitrariness of $\xi^{(2)}$ results from there being no surface mass density.

This completes the derivation of the contracted FDT for Brownian motion.

APPENDIX A

Assume that P commutes with P_α, R_α^{-1}, and R^{-1}. With this assumption we prove the OCR given in the text in Eq. (31).

Let J be given by

$$J = \int dt \frac{d}{dt} [b^{(1)}(t)^T S_p^{-1} b^{(2)}(T - t)] \tag{A1}$$

Because $b^{(1)}(t)$ and $b^{(2)}(t)$ vanish for $t < -T_c$, J vanishes. Using the contracted equations of motion, the differentiation in the integrand of Eq. (A1) can be performed, giving

$$\begin{aligned} 0 = \int dt \,\{ & b^{(1)}(t)^T(\Omega^T S_p^{-1} - S_p^{-1}\Omega) b^{(2)}(T - t) \\ & - [f^{(1)}(t)^T S_p^{-1} b^{(2)}(T - t) - b^{(1)}(t)^T S_p^{-1} f^{(2)}(T - t)]\} \\ & + \int dt \int ds\, [b^{(1)}(s)^T \Gamma^T(t - s) S_p^{-1} b^{(2)}(T - t) \\ & - b^{(1)}(t)^T S_p^{-1} \Gamma(T - t - s) b^{(2)}(s)] \end{aligned} \tag{A2}$$

In the second double integral let $T - s \to z$, $t \to s$, and $z \to t$. Then Eq. (A2) becomes

$$\begin{aligned} 0 = \int dt \int ds\, (& b^{(1)}(s)^T\{\delta(t - s)[\Omega^T S_p^{-1} - S_p^{-1}\Omega] \\ & + [\Gamma^T(t - s) S_p^{-1} - S_p^{-1}\Gamma(s - t)]\} b^{(2)}(T - t)) \\ & - \int dt\, [f^{(1)}(t)^T S_p^{-1} b^{(2)}(T - t) - b^{(1)}(t)^T S_p^{-1} f^{(2)}(T - t)] \end{aligned} \tag{A3}$$

We are free to choose $F^{(1)}$ and $F^{(2)}$ at will. We choose these forces such that $QF^{(1)} = QF^{(2)} = 0$ and $f^{(1)} = PF^{(1)}$; $f^{(2)} = PF^{(2)}$. Then the last integral of Eq. (A3) becomes

$$\int [F^{(1)}(t)^T S^{-1} a^{(2)}(T - t) - a^{(1)}(t)^T S^{-1} F^{(2)}(T - t)]\, dt \tag{A4}$$

because the commutator of P with S^{-1} vanishes. The original, noncontracted OCR, Eq. (18), shows that the expression given in Eq. (A4) vanishes. This means that the double integral in Eq. (A3) vanishes for arbitrarily driven

$b^{(1)}(t)$ and $b^{(2)}(t)$. This in turn implies the contracted OCR, Eq. (31). The solutions $b^{(1)}(t)$ and $b^{(2)}(t)$ are used as test functions here.

APPENDIX B

In this appendix we give a proof of Eq. (32) in the text. We begin by noting that the integral J given in Eq. (A1) vanishes for arbitrary $b^{(1)}(t)$ because $b^{(2)}(t)$ vanishes at both ends of the integration. In particular, if we replace $b^{(1)}(t)$ by the fluctuating quantity $b(t)$ we have

$$0 = J' = \int dt \frac{d}{dt} [b(t)^T S_p^{-1} b^{(2)}(T - t)] \tag{B1}$$

Again, as in Appendix A, use the contracted equation of motion to perform the differentiation in the integrand. This procedure yields

$$\begin{aligned} 0 = \int dt \int ds \, (b(s)^T \{[\Omega^T S_p^{-1} - S_p^{-1}\Omega] \, \delta(t - s) \\ + [\Gamma^T(t - s) S_p^{-1} - S_p^{-1}\Gamma(s - t)]\} b^{(2)}(T - t)) \\ - \int dt \, [h(t)^T S_p^{-1} b^{(2)}(T - t) - b(t)^T S_p^{-1} f^{(2)}(T - t)] \end{aligned} \tag{B2}$$

The double integral has been treated in the same way that we treated the double integral of Appendix A. Now, however, we can use the result of Appendix A, the contracted OCR, to show that the first integrals in Eq. (B2) vanish, leaving

$$\int dt \, h(t)^T S_p^{-1} b^{(2)}(T - t) = \int dt \, b(t)^T S_p^{-1} f^{(2)}(T - t) \tag{B3}$$

By assumption $f^{(2)} = PF^{(2)}$, and this means that the right side of Eq. (B3) becomes

$$\begin{aligned} \int dt \, b(t)^T S_p^{-1} f^{(2)}(T - t) &= \int dt \, b(t)^T S_p^{-1} F^{(2)}(T - t) \\ &= \int dt \, a(t)^T S_p^{-1} F^{(2)}(T - t) \\ &= \int dt \, a(t)^T S^{-1} F^{(2)} \end{aligned} \tag{B4}$$

These equalities follow from the definitions

$$S_p^{-1} = PS^{-1}P \qquad \text{and} \qquad b(t) = Pa(t)$$

and the assumption that P commutes with R^{-1}. Combining Eqs. (B3), (B4), and (B2) gives Eq. (32).

APPENDIX C

In this appendix we give a few of the details leading to Eq. (58). First consider the integral I_1 given by

$$\begin{aligned} I_1 &= \int dt \int d^3r \, [\nabla\cdot\mathbf{g}^{(1)}T^{(2)} - T^{(1)}\,\nabla\cdot\mathbf{g}^{(2)}] \\ &= \int dt \int d^3r \, \frac{\rho_0 c_v}{T_0}\left\{\left[\frac{\partial T^{(1)}}{\partial t} + \frac{\alpha T_0}{\rho_0 c_v \chi_T}\,\nabla\cdot\mathbf{u}^{(1)} + \frac{1}{\rho_0 c_v}\,\nabla\cdot\mathbf{q}^{(1)}\right]T^{(2)}\right. \\ &\quad \left. - T^{(1)}\left[\frac{\partial T^{(2)}}{\partial t} + \frac{\alpha T_0}{\rho_0 c_v \chi_T}\,\nabla\cdot\mathbf{u}^{(2)} + \frac{1}{\rho_0 c_v}\,\nabla\cdot\mathbf{q}^{(1)}\right]\right\} \end{aligned} \tag{C1}$$

Quantities with superscript (1) are understood to have arguments $(\mathbf{r}, t)$; those with superscript (2) have arguments $(\mathbf{r}, T - t)$. The time derivatives combine to give $(\partial/\partial t)(T^{(1)}T^{(2)})$ and, as usual, integrals involving these terms vanish. The integral I_1 thus reduces to

$$\begin{aligned} I_1 &= \int dt \int d^3r \, \{(\alpha/\chi_T)[\nabla\cdot\mathbf{u}^{(1)}T^{(2)} - T^{(1)}\,\nabla\cdot\mathbf{u}^{(2)}] \\ &\quad \times (1/T_0)[\nabla\cdot\mathbf{q}^{(1)}T^{(2)} - T^{(1)}\,\nabla\cdot\mathbf{q}^{(2)}]\} \end{aligned} \tag{C2}$$

Let the integral I_2 be given by

$$\begin{aligned} I_2 &= \int dt \int d^3r \, [-\nabla\cdot\mathsf{s}^{(1)}\cdot\mathbf{u}^{(2)} + \mathbf{u}^{(1)}\cdot\nabla\cdot\mathsf{s}^{(2)}] \\ &= \int dt \int d^3r \left\{\rho_0\left[\frac{\partial\mathbf{u}^{(2)}}{\partial t}\cdot\mathbf{u}^{(1)} - \mathbf{u}^{(2)}\cdot\frac{\partial\mathbf{u}^{(1)}}{\partial t}\right]\right. \\ &\quad \left. + [\nabla\cdot\mathsf{P}^{(1)}\cdot\mathbf{u}^{(2)} - \mathbf{u}^{(1)}\cdot\nabla\cdot\mathsf{P}^{(2)}]\right\} \end{aligned} \tag{C3}$$

Again the first terms vanish. Integrating by parts gives

$$\begin{aligned} I_2 &= \int dt \int dS \, [\hat{\mathbf{n}}\cdot\mathsf{P}^{(1)}\cdot\mathbf{u}^{(2)} - \mathbf{u}^{(1)}\cdot\mathsf{P}^{(2)}\cdot\hat{\mathbf{n}}] \\ &\quad + \int d^3r \, [-\mathsf{P}^{(1)}:\nabla\mathbf{u}^{(2)} + \nabla\mathbf{u}^{(1)}:\mathsf{P}^{(2)}] \end{aligned} \tag{C4}$$

Even though there is a singularity in the pressure tensor at the particle surface, the stress tensors appearing here are the same as those appearing in the equations of motion of the particle. The reason is that there is no surface mass density and momentum must be conserved.

We define the integral I_3 by

$$I_3 = -\int dt\, [\mathbf{F}^{(1)}\cdot\mathbf{U}^{(2)} + \mathbf{M}^{(1)}\cdot\boldsymbol{\Omega}^{(2)} - \mathbf{U}^{(1)}\cdot\mathbf{F}^{(2)} - \boldsymbol{\Omega}^{(1)}\cdot\mathbf{M}^{(2)}]$$

$$= -\int dt \int d^2S\, [\hat{\mathbf{n}}\cdot\mathsf{P}^{(1)}\cdot\mathbf{U}^{(2)} + (\boldsymbol{\Omega}^{(2)}\times\mathbf{r})\cdot\mathsf{P}^{(1)}\cdot\hat{\mathbf{n}}$$

$$- \mathbf{U}^{(1)}\cdot\mathsf{P}^{(2)}\cdot\hat{\mathbf{n}} - (\boldsymbol{\Omega}^{(1)}\times\mathbf{r})\cdot\mathsf{P}^{(2)}\cdot\hat{\mathbf{n}}] \tag{C5}$$

With these definitions, Eq. (57) can be written as

$$0 = I_1 + I_2 + I_3$$

$$= \int dt \Bigg\{ \int d^3r\, [(\alpha/\chi_T)(\nabla\cdot\mathbf{u}^{(1)}T^{(2)} - T^{(1)}\,\nabla\cdot\mathbf{u}^{(2)})$$

$$+ (1/T_0)(\nabla\cdot\mathbf{q}^{(1)}T^{(2)} - T^{(1)}\,\nabla\cdot\mathbf{q}^{(2)}) - (\mathsf{P}^{(1)}:\nabla\mathbf{u}^{(2)} - \nabla\mathbf{u}^{(1)}:\mathsf{P}^{(2)})]$$

$$+ \int dS\, [\hat{\mathbf{n}}\cdot\mathsf{P}^{(1)}\cdot\boldsymbol{\Delta}^{(2)} - \boldsymbol{\Delta}^{(1)}\cdot\mathsf{P}^{(2)}\cdot\hat{\mathbf{n}}]\Bigg\} \tag{C6}$$

where

$$\boldsymbol{\Delta}^{(i)}(\mathbf{r}, t) = \mathbf{u}^{(i)}(\mathbf{r}, t) - \mathbf{U}^{(i)}(t) - \boldsymbol{\Omega}^{(i)}\times\mathbf{r}, \qquad \mathbf{r}\in S, \quad i = 1, 2$$

Now examine the quantity I_4 which appears in Eq. (C6) and is given by

$$I_4 = \int dt \int d^3r\, [\mathsf{P}^{(1)}:\nabla\mathbf{u}^{(2)} - \nabla\mathbf{u}^{(1)}:\mathsf{P}^{(2)}]$$

$$= \int dt \int d^3r\, [-p^{(1)}\,\nabla\cdot\mathbf{u}^{(2)} + \nabla\cdot\mathbf{u}^{(1)}p^{(2)} + \sigma^{(1)}:\nabla\mathbf{u}^{(2)} - \nabla\mathbf{u}^{(1)}:\sigma^{(2)}] \tag{C7}$$

In Equation (C7), $p^{(i)}(r, t)$ is given by the equation of state

$$p(\mathbf{r}, t) = (\alpha/\chi_T)T(\mathbf{r}, t) + \rho_0 \int d^3r'\, Q(\mathbf{r}, \mathbf{r}')(\mathbf{r}', t) \tag{C8}$$

The kernel $Q(\mathbf{r}, \mathbf{r}')$ can be assumed to be a symmetric function of its arguments. The contribution of terms involving $Q(\mathbf{r}, \mathbf{r}')$ to I_4 is

$$\int dt \int d^3r \int d^3r' \Bigg[- Q(\mathbf{r}, \mathbf{r}')\rho^{(1)}(\mathbf{r}', t)\,\frac{\partial\rho^{(2)}}{\partial t}(\mathbf{r}, T - t)$$

$$+ \frac{\partial\rho^{(1)}}{\partial t}(\mathbf{r}, t)Q(\mathbf{r}, \mathbf{r}')\rho^{(2)}(\mathbf{r}', T - t)\Bigg]$$

$$= -\int dt\, \frac{d}{dt} \int d^3r \int d^3r'\, \rho^{(1)}(\mathbf{r}, t)Q(\mathbf{r}, \mathbf{r}')\rho^{(2)}(\mathbf{r}', T - t) = 0 \tag{C9}$$

Therefore Eq. (C7) becomes

$$I_4 = \int dt \int d^3r \, [-(\alpha/\chi_T)(T^{(1)} \nabla\cdot\mathbf{u}^{(2)} - \nabla\cdot\mathbf{u}^{(1)}T^{(2)}) \\ + (\sigma^{(1)}\mathbf{:}\nabla\mathbf{u}^{(2)} - \nabla\mathbf{u}^{(1)}\mathbf{:}\sigma^{(2)})]$$

Using the result in Eq. (C6) and integrating terms involving $\nabla\cdot\mathbf{q}$ by parts gives Eq. (58) of the text.

ACKNOWLEDGMENTS

The author thanks Prof. E. H. Hauge for suggesting the problem considered here. He also thanks Norges Teknisk-Naturvitenskapilige Forskningsråd for the postdoctoral fellowship which enabled him to undertake this work at the Institute for Theoretical Physics at NTH, Trondheim, Norway.

REFERENCES

1. R. F. Fox and G. E. Uhlenbeck, *Phys. Fluids* **13**:1893 (1970).
2. E. H. Hauge and A. Martin-Löf, *J. Stat. Phys.* **7**:259 (1973).
3. D. Bedeaux and P. Mazur, *Physica* **76**:247 (1974).
4. M. G. Velarde and E. H. Hauge, *J. Stat. Phys.* **10**:103 (1974).
5. T. S. Chow and J. J. Hermans, *Physica* **65**:156 (1973).
6. D. Bedeaux, A. M. Albano, and P. Mazur, *Physica* **88A**:574 (1977).
7. M. Gitterman, *Rev. Mod. Phys.* **50**:85 (1978).
8. S. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), Chapter VIII; see also H. B. G. Casimir, *Rev. Mod. Phys.* **17**:343 (1945).
9. R. F. Fox, *J. Stat. Phys.* **16**:259 (1977); *J. Math. Phys.* **18**:2331 (1977).
10. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Reading, Mass., 1975), Chapter 6.
11. M. S. Gitterman and V. M. Kontorovich, *Sov. Phys.—JETP* **20**:1433 (1965).
12. T. C. Lubensky and M. H. Rubin, *Phys. Rev. B* **12**:3885 (1975).